

Effect of dicarboxylic acid esters on the lubricity of aviation kerosene for use in CI engines

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Abstract: To reduce their fuel related logistic burden, North Atlantic Treaty Organization (NATO) Armed Forces are advancing the use of a single fuel for both aircraft and ground equipment. To this end, F-34 (the commercial equivalent is Jet A-1) is replacing distillate diesel fuel in many applications. However, tests conducted with this kerosene type on high frequency reciprocating rig showed that this type of fuel causes unacceptable wear. This excessive wear is caused by the poor lubricity of aviation fuel. In order to make this type of fuel compatible with direct injection compression engines, seven di-carboxylic acid esters have tested to improve the lubricity of kerosene. Tribological results showed that all esters tested in this series of experiments seem to be suitable for increasing the kerosene lubricity to a satisfactory level.

Keywords: lubricity; aviation kerosene; F-34; Jet A-1; compression ignition (CI) engines; dicarboxylic acid esters

1 Introduction

The idea of using one military fuel on the battlefield was conceived after the second world war, in order to simplify the logistic supply chain for petroleum products. Whilst two North Atlantic Treaty Organization (NATO) nations had converted to F-34 (comparable with commercial aviation fuel Jet A-1) in the mid-1960's, the move towards a single military fuel for the battlefield began in the 1970's when NATO Air Forces agreed to change their operating fuel from the wide cut F-40 (JP-4) to the safer, less flammable kerosene fuel F-34 (JP-8). One of the main reasons for this change was improved flight and ground based largely on US experiences during the Vietnam War [1].

In 1988, NATO nations decided to move towards the use of a single fuel (JP-8) for all land-based military aircraft, vehicles and equipment when employed on the European battlefield; this idea has become to be

referred to as the single fuel concept (SFC) [2]. The logic behind such a decision comes not only from the gain of big logistical prizes in war time, but also from the more pragmatic fact of being able to both simplify and make better use of the NATO extensive and expensive pipeline system in times of peace [3]. The single fuel selected has been the F-34 (JP-8) military jet kerosene which is based upon the civil jet fuel F-35 (Jet A-1), which is widely available throughout the European Arena, with the inclusion of a military additive possessing anti-icing properties [4].

Prior to the decision, member nations of NATO have undertaken studies in order to identify problems that could arise in practice by the use of the kerosene based fuel in diesel engine vehicles (tanks, transporters, etc.) [5].

The accumulation of such experiences gained from these peace time studies was sufficient for the application of the concept to be tested in the war zone during the "Desert Storm" battle [6]. Although sufficient experience was gained, it was considered by NATO that further studies and exchange of

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experience should take place between the member nations in order to identify areas of development and activities required in order to better understand the engine operation with F-34 (JP-8) fuel; the latter one would eventually lead to resolving of the identified operational difficulties [7–9].

However, one main problem was identified in the process of implementing the SFC. In general, F-34 or the similar product F-35 showed a lower lubricity than commercial distillate diesel fuels. This may be because diesel fuel, having a higher boiling temperature range than kerosene, contains a larger proportion of naturally-occurring lubricity agents [10].

The objective of this work was to assess the lubricating properties of low sulfur diesel fuels additized with seven esters of mono-carboxylic acids of different structure. Data were generated to identify the minimum concentration of the above oxygen containing compounds, which provide lubricity improvement down to the 460 μm wear scar diameter level. The value of 460 μm was proposed by the European Committee for Standardization (CEN) in February 1997, and generally adopted by the industry, as the minimum requirement for an acceptable field performance [11].

Oxygen containing compounds such as fatty acids and their derivatives are superior friction reducing agents [12–24]. These compounds adsorb or react on rubbing surfaces to reduce adhesion between contacting asperities and limit friction, wear and seizure. Wei and Spikes considered that the significant wear reduction was produced by oxygen compounds with phenolic-type or carboxylic acid groups and occurred at a concentration of just a few parts per million [25]. On the other hand the use of oxygen containing fuels, such as esters, assists in the reduction of particulate matter emissions. More generally, it has been mentioned in the literature that the oxygen–carbon ratio (O/C) of a fuel significantly affects particulate emissions; so to achieve low smoke emissions (lower than 0.5 in the Bosch range), the O/C ratio must be higher than 0.2 [26].

Although the impact of fatty acid esters on the lubricity of automotive diesel has been closely examined, their impact on the tribological properties of aviation fuels for use in compression ignition engines has not been examined in detail.

2 Experimental procedure

To assess the impact of the selected oxygen components on the lubrication properties of kerosene, an aviation fuel was obtained by a Greek refinery and was used for all the tribological experiments as a base fuel. The fuel properties are presented in Table 1, along with the standard methods that were used for their determination.

All tribological measurements were carried out using the high frequency reciprocating rig (HFRR) apparatus (Fig. 1), according to the CEC F-06-A-96 method. The test temperature was 60 °C and the volume of the fuel sample used was 2 ml. Relative humidity was kept between 55%–58%, while the mean ambient temperature was 24 °C. The lubricating efficiency of the fuels was estimated by measuring the; photo-microscope. The wear scars quoted are corrected to give wear scar (WS) 1.4 values. The repeatability was calculated using the following equation [27]:

$$R = 139 - (0.1648 \times \text{WS}1.4) \quad (1)$$

The esters of di-carboxylic acids that were not

Table 1 Properties of aviation fuel.

Fuel type	JP-8	Method
Density (gr/ml, 15 °C)	0.7950	ASTM D 1298 [28]
Viscosity (cSt, −20 °C)	3,87	ASTM D 445 [29]
Flash point (°C)	41	ASTM D 93 [30]
Conductivity (pS/m)	375	ASTM D 2624 [31]
Sulfur wt%	0.23	ASTM D 4294 [32]
Aromatics vol%	15.3	ASTM D 1319 [33]
Olefins vol%	0.3	ASTM D 1319 [33]
Lubricity		
Initial measurement (μm)	754	CEC F-06-A-96 [27]
Repeated measurement (μm)	758	
Distillation (°C)		
Ignition bioling point (IBP)	145	ASTM D 86 [34]
10%	174	
20%	181	
50%	200	
90%	233	
Final boiling point (FBP)	250	

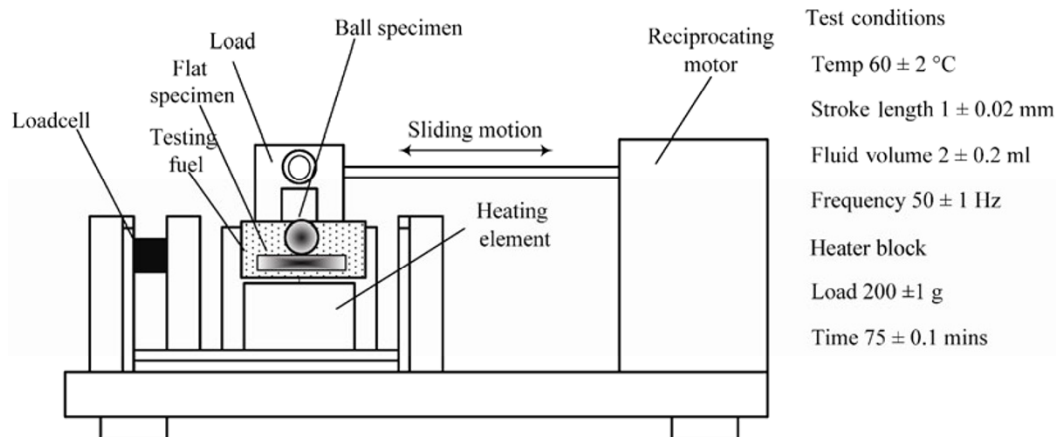
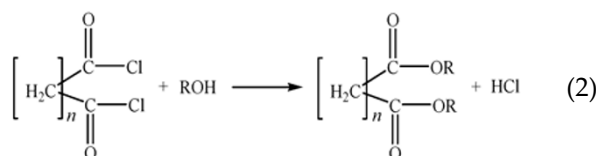


Fig. 1 Schematic diagram of lubricity test by high frequency reciprocating test rig.

commercially available were prepared by reacting di-chlorides of carboxylic acids with alcohols. The reaction can be expressed by the following equation:



The alcohols and small excesses of triethylamine were dissolved in toluene, followed by the gradual addition of 0.7 mol equivalent of the acid di-chlorides with continuous stirring and cooling. The mixtures were stirred at room temperature for 24 h. Afterward, they were washed with ice cold water, HCl 0.01 N and 5% aqueous sodium bicarbonate. The organic phases were dried over anhydrous sodium sulfate and finally the residues were distilled on a vacuum evaporator to receive the final products, whose

properties were similar to those reported in the relevant literature [35–41]. In an effort to establish the purity of the prepared compounds, elemental analysis was carried out using the CHNS-O Carlo Erba EA1108 elemental analyzer of the laboratory, and the results are given in Table 2. The lack of structure indicator instrument keeps down any further information and transfers the continuation this part of the research for the near future. When the measured properties of the density d_4^{20} , the refractive index n_D^{20} (Table 3), and the elemental analysis are compared to the corresponding data found in literature, the purity level of the compounds eventually used in this study, was estimated to be at least 90%.

The seven esters of di-carboxylic acids were dissolved to the base fuel, at the same concentration levels, i.e., 200, 400, 600, 800, 1,000, 1,200, 1,400, and 1,600 ppm.

Table 2 Elemental analysis of the oxygen compounds.

Nomenclature	Calculated content of C, H, O (%)			Estimated content of C, H, O (%)		
	C	H	O	C	H	O
Dibutyl adipate	65.1	10.1	24.8	64.9	10.1	24.7
Dioctyl adipate	71.3	11.3	17.3	71.6	11.5	17.1
Diethyl azelate	63.9	9.83	26.2	64.0	10.0	26.5
Dibutyl azelate	68.0	10.6	21.3	67.8	10.2	21.2
Dioctyl azelate	72.8	11.6	15.5	73.1	11.7	15.5
Diethyl sebacate	65.1	10.1	26.8	64.9	10.4	26.7
Bis(2-ethyl-hexyl) sebacate	73.2	11.7	15.0	73.1	11.5	14.8

Table 3 Characteristics of the oxygen compounds.

Nomenclature	Chemical structure	Molecular weight	Measured density, d_4^{20}	Density of pure ester, d_4^{20}	Measured refractive index, n_D^{20}	Refractive index of pure ester, n_D^{20}
Dibutyl adipate	$C_{14}H_{26}O_4$	258	0.941	0.945 [35]	1.4364	1.4358 [35]
Dioctyl adipate	$C_{22}H_{42}O_4$	370	0.930	0.925 [36]	1.4478	1.4471 [36]
Diethyl azelate	$C_{13}H_{24}O_4$	244	0.968	0.973 [37]	1.4356	1.4350 [37]
Dibutyl azelate	$C_{17}H_{32}O_4$	300	0.942	0.947 [38]	1.4412	1.4406 [38]
Dioctyl azelate	$C_{25}H_{48}O_4$	412	0.913	0.918 [39]	1.4518	1.4510 [39]
Diethyl sebacate	$C_{14}H_{26}O_4$	258	0.991	1.007 [40]	1.4369	1.4360 [40]
Bis(2-ethyl-hexyl) sebacate	$C_{26}H_{50}O_4$	426	0.924	0.919 [41]	1.4516	1.4510 [41]

3 Results and discussion

The base fuel was initially analyzed to determine its lubrication effectiveness. The corrected wear scar diameter (WSD) value for the base fuel, on the first day of its production, is cited in Table 1. It is evident that the fuel has a wear scar diameter value much higher than the acceptable limit of 460 μm , and was characterized as fuel with poor lubricating properties. Repeated tribological measurement on the next day confirmed this conclusion. Consequently, this fuel was well suited to determine the lubricity of additives.

Figure 2 gives, in graphical form, the effect of the addition of dibutyl adipate on the WS1.4 of the base fuel. Small concentrations of dibutyl adipate that

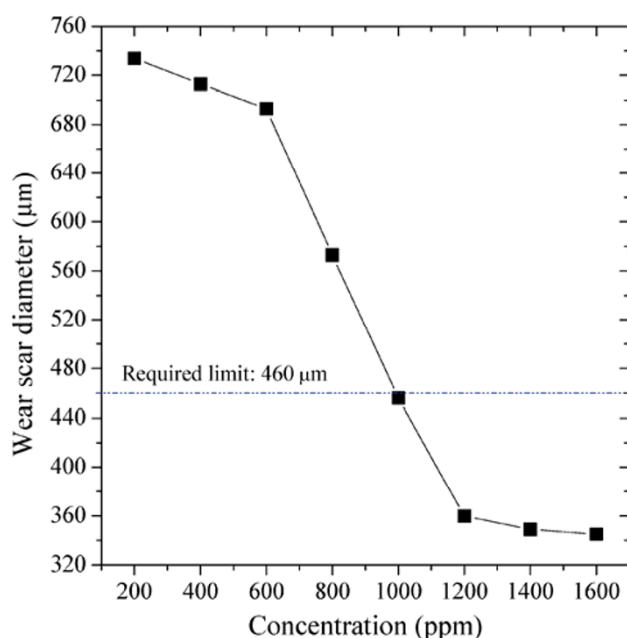


Fig. 2 Impact of dibutyl adipate addition on the lubrication properties of the F-34 military jet kerosene.

ranged between 200 and 600 ppm practically caused no alteration on the corrected wear scar diameter of the base fuel. A substantial increase of the lubrication performance was shown with the addition of the dibutyl adipate under observation in the concentration of 800 ppm. Yet, even in this case, the limit of 460 μm was not satisfied. When dealing with the increase of the concentration of dibutyl adipate from 800 to 1,000 ppm, it was observed that there was an increasing effect on the lubricity of the base fuel, thus decreasing the wear scar diameter by 4 μm under the acceptable limit. For concentrations of dibutyl adipate between 1,200 and 1,600 ppm the decrease in the WSD values was small, and the fuel attained a constant wear scar diameter value of approximately 350 μm .

The impact of dioctyl adipate on the lubricity of the base fuel is outlined in Fig. 3. When analyzing the results, it is observed that the addition of dioctyl adipate in the concentrations between 200 and 600 ppm even though it increased the lubricity of the base fuel, it did not reach the acceptable limit value of 460 μm . The desired improvement was realized as there was an increase in the concentration of dioctyl adipate from 600 to 800 where the maximum permissible HFRR mean wear scar diameter of 460 μm , required for commercial diesel fuels was satisfied. Comparing the tribological results of dioctyl adipate with those of dibutyl adipate, it is observed that the first has a better lubricating behavior on the base fuel.

Figure 4 shows the influence of diethyl azelate on the lubrication properties of the base fuel. On the basis of the HFRR test results, the addition of diethyl azelate at the concentration levels lower than 1,000 ppm

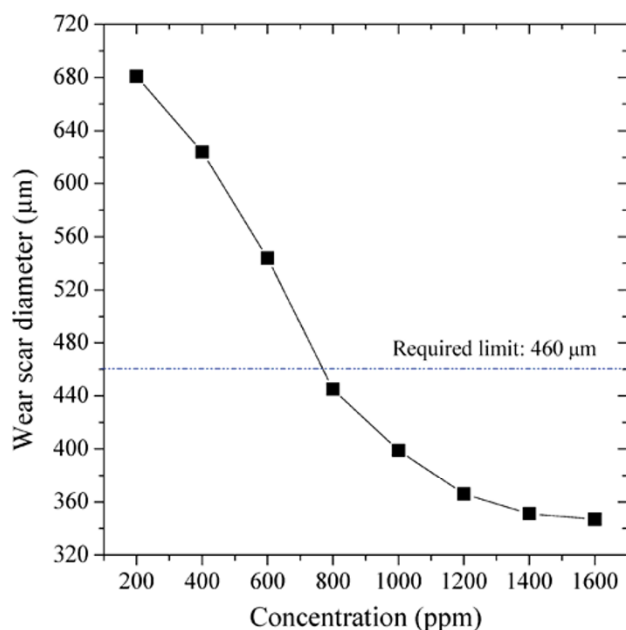


Fig. 3 Impact of dioctyl adipate addition on the lubrication properties of the F-34 military jet kerosene.

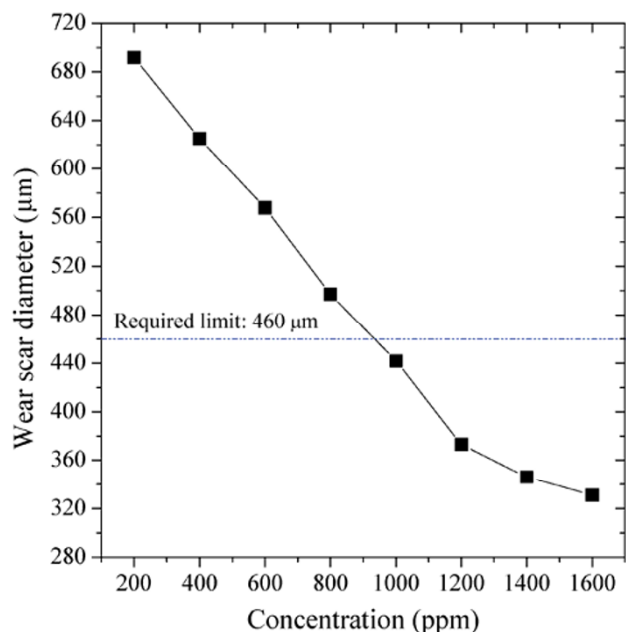


Fig. 4 Impact of diethyl azelate addition on the lubrication properties of the F-34 military jet kerosene.

does not seem capable to increase the lubricity of the fuel to an acceptable level. Contrary, a significant reduction on the WS1.4 to under the limit of 460 μm is observed when 1,000 ppm of diethyl azelate is added, whereas extra addition of same dicarboxylic acid ester seems to offer even better improvement on

the lubrication properties of the base fuel. Thus, for concentrations between 1,200 and 1,600 ppm, the WSD illustrates an even higher decline, reaching 331 μm .

Figure 5 depicts the impact of the addition of dibutyl azelate on the base fuel lubricity. As in the case of diethyl azelate (Fig. 3), similarly here, the required treat rate to obtain a satisfactory wear scar diameter (WS1.4) of 460 μm was 1,000 ppm. However, a higher dosage of dibutyl azelate led to a slight increase of the fuel lubricity. The careful assessment of the experimental results leads to the realization that dibutyl azelate presents a slightly improved lubrication performance than diethyl azelate. Even though, both types of dicarboxylic acid esters provide an acceptable level of performance at a 1,000 ppm, however at this concentration level, the corrected wear scar diameter of diethyl azelate was 442 μm , while the WSD value of the dibutyl azelate was 429 μm . Thus the second dicarboxylic acid ester had a slightly better lubrication performance.

Figure 6 presents the dependence of the base fuel lubricity on the concentration of dioctyl azelate. Although its addition at concentrations lower than 800 ppm did not seem capable to set the WS1.4 value well within the required limit, however a notable improvement in the fuel lubricity was observed with

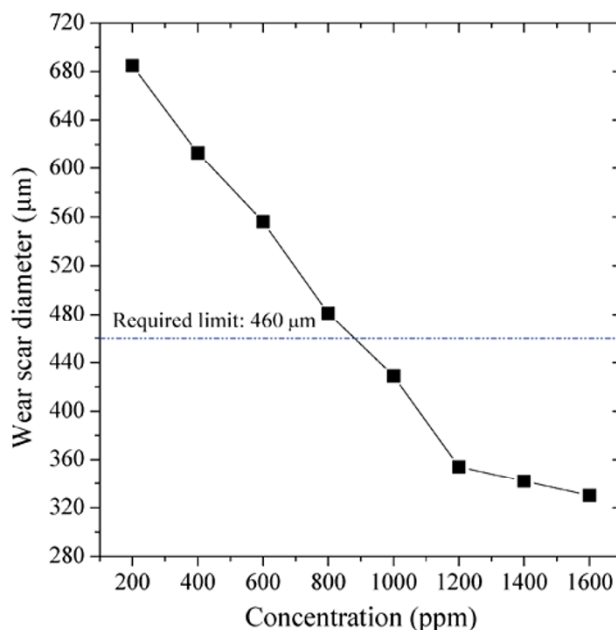


Fig. 5 Impact of dibutyl azelate addition on the lubrication properties of the F-34 military jet kerosene.

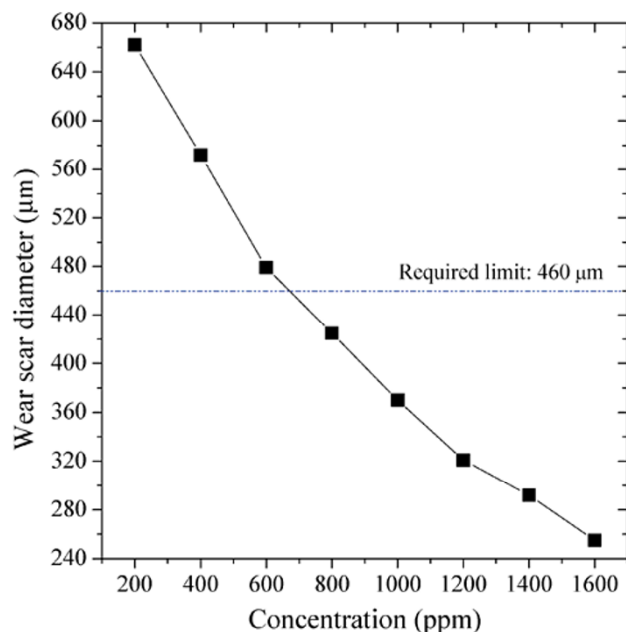


Fig. 6 Impact of dioctyl azelate addition on the lubrication properties of the F-34 military jet kerosene.

the addition of 800 ppm of dioctyl azelate, where the wear scar diameter was decreased to 425 μm . It should also be noted that this ester presented the best effect on the lubrication properties of the base fuel from any other type of dicarboxylic acid ester that was examined.

Figures 7 and 8 illustrate the lubricity improvement due to the addition of diethyl sebacate and bis(2-ethyl-hexyl) sebacate to the base fuel. Here the required treat rates to obtain a satisfactory wear scar diameter (WS1.4) of 460 μm , were 1,000 and 800 ppm respectively.

It is evident that, in order to improve the lubrication properties of kerosene, small concentration levels of di-carboxylic esters ranging from 800–1,000 ppm, were necessary to bring the wear scar diameter value within the required limit, and any extra addition of di-carboxylic acid esters, did not give any significant improvement in the lubricity of the fuels.

Although, all types of the di-carboxylic esters tested in this series of experiments, had a beneficial impact on the lubricity of kerosene, an interesting conclusion is derived from the comparison of diesters produced from the same di-carboxylic acid. Among the diesters derived from the same di-carboxylic acid, i.e. the adipate and azelate series, an increase of the

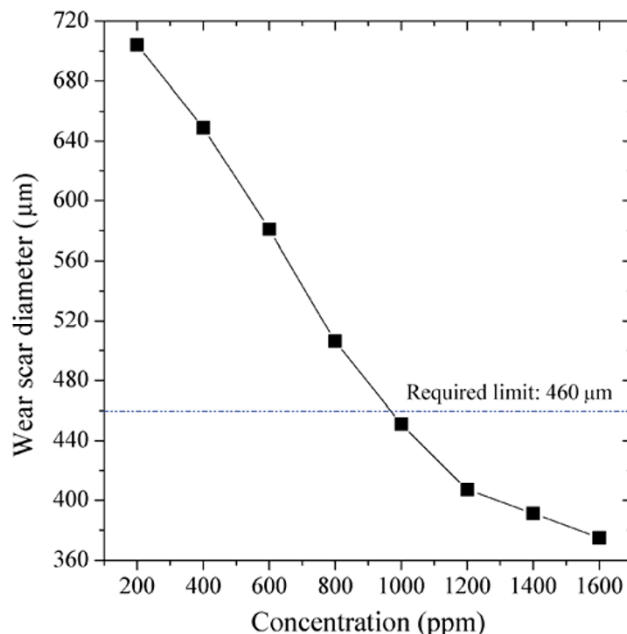


Fig. 7 Impact of diethyl sebacate addition on the lubrication properties of the F-34 military jet kerosene.

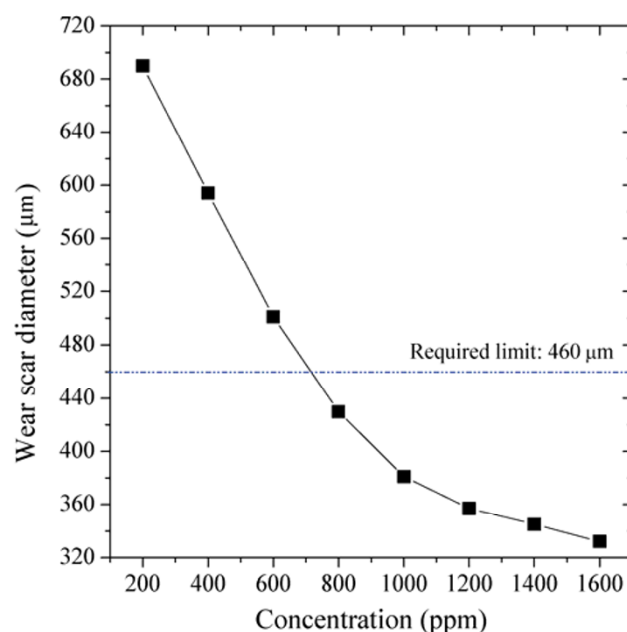


Fig. 8 Impact of bis(2-ethyl-hexyl) sebacate addition on the lubrication properties of the F-34 military jet kerosene.

chain length of the alcohol involved in the esterification reaction, namely from diethyl to dibutyl and dioctyl alcohol, leads to a higher lubrication performance; conversely, if the chain length of the alcohol is kept constant, an increase in dicarboxylic

acid chain length does not cause significant improvement in lubricity.

4 Conclusions

In an effort to investigate the impact of mono-carboxylic acid esters on the tribological properties of kerosene, seven esters were added to a military aviation fuel JP-8. The following conclusions can be drawn from this study:

1. Current aviation kerosene, when used in army ground vehicles as part of the single fuel concept, does not provide satisfactory lubrication and may lead to damage in the fuel pumps of the engines.

2. Small concentration levels of the mono-carboxylic acid esters ranging from 800–1,000 ppm, were necessary to bring the wear scar diameter value within the required limit of 460 μm , and any extra addition of the esters, did not give any significant improvement in the lubricity of the fuels.

3. Among the esters of the same molecular type, those having the ester group around the middle of the molecule appear to give a better lubrication performance.

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